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Improved Hydrotalcite-type Compounds for Post-Combustion CO_2 Abatement

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Abstract

Among the greenhouse gasses, CO_2 emissions are of great concern. Releasing 4Gt fossil carbon results in an annual increase in the atmospheric concentration of CO_2 by 1 ppm. As the demand for fuel increases progressively with worldwide economic progress, CO_2 emissions become a stringent problem; scientists are looking for solutions to deal with this problem. CO_2 capture and storage is one of the only viable options for capturing CO_2 emissions from stationary point sources. Post-combustion CO_2 capture systems could be retrofit to existing and new point CO_2 sources, such as power plants. The current state of the art technology utilizes an aqueous amine solution in a temperature swing for CO_2 capture. There are several potential advantages of using solid materials, such as a lower specific heat capacity and less evaporation of moisture. However, significant improvements in sorbent performance are still necessary. Specifically, the cost, stability, attrition, and interaction with flue gas constituents are of concern.

This work exploits the possibility to change the characteristics of the hydrotalcite-type materials by increasing their CO_2 physisorption properties in order to make them more suitable for the post-combustion technologies. By inducing changes during the preparation of hydrotalcite-type compounds and/or addition of dopants such as Zr^{4+} it has been possible to modify the structure of these materials by lowering the strength of the water bonding to the surface of the material. This leads to the decrease of the temperature where the dehydration takes place. Moreover, this gives higher than normal CO_2 capacities at low temperatures which are explained through the existence of weak basic sites. This behaviour is temperature dependent and gives scope to exploit the structural characteristics of the hydrotalcite type compounds for developing new materials which to compete with amine based systems in terms of energy efficiency.

The hydrotalcites have been evaluated at the laboratory scale. The importance of activation temperature, moisture, and testing procedure has been highlighted. The deactivation is only related to the dehydration process and the process is reversible as no structural modification at the level of octahedral layers can be observed.

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1. Introduction

Carbon dioxide capture and storage (CCS) can be an important component of reducing worldwide CO_2 emissions from stationary point sources, such as coal-fired power plants [1-3]. For the entire process of carbon capture and storage, the capture step is the most expensive, and therefore this step receives more interest for potential cost reductions. The state of the art capture CO_2 technology utilizes aqueous monoethanol amine (MEA) in a temperature swing process. Dry sorbents can also be used for temperature swing adsorption (TSA), but may lead to significant cost reductions for CO_2 capture, for many reasons, such as lower specific heat and less evaporation of water; the sensible heat requirement and latent heat requirement for aqueous MEA are both significant [4]. Using dry sorbents can significantly reduce this energy penalty, depending on the sorbent's propensity to adsorb water. In addition, amines can degrade at high temperatures, but some dry sorbents have the ability to withstand significant higher temperatures, which could reduce the size of the regenerator and thus reduce capital costs.

There are several potential classes of sorbents that could be viable for post-combustion CO_2 capture, such as zeolites, activated carbons, hydrotalcites, supported amines, supported carbonates, functionalized metal organic frameworks, etc. [5,6] Hydrotalcites are of particular interest because they are not as sensitive to high temperatures, and therefore could potentially be used in a TSA process where the reactor sizes could be significantly smaller.

Hydrotalcites, from the anionic clay class, have a positively charged brucite layers that leads to characteristics such as adsorption capacity, the mobility of anions and H_2O molecules, large surface areas and stability. The positive charge in the brucite layers are attributed to trivalent cations replacing the divalent cations in the centre of the octahedral sites. Consequently there is a net charge on the layer which is compensated by a layer of anions. The different ratios of trivalent and divalent cations can increase or decrease the CO_2 adsorption capacity, as well as changing the types of anions found in the structure. Hydrotalcites CO_2 adsorption also increases when in the presence of H_2O. CO_2 sorption properties of the hydrotalcite type compounds are based on the retro-topotactical transformation or memory effect property shown by these materials. When calcined, hydrotalcite-type compounds are able to recover their initial layered structure if put in contact with water and appropriate anions.

It is suggested that the presence of moisture protects the surface area from being damaged. This allows for a higher activation temperature which in turn activates a larger amount of adsorption sites. In the lab, hydrotalcites have been found to be able to regenerate adsorbed CO_2 under a N_2 gas purge at an increased temperature.

The acidic CO_2 molecules can be adsorbed onto this type of materials at the level of interlayer space leading to their structural reconstruction. CO_2 is used as probe molecule to investigate the basicity of these materials. Its acidity has enough strength to probe all the basic sites through the formation of several carbonate species. According to multiple studies monodentate, bidentate and bicarbonate anions can be detected by IR spectroscopy [7-9] in the 1700-1300cm^{-1} region. Monodentate carbonate are linked with the strong basic sites through the involvement of low-coordination oxygen [10]. Bidentate carbonates aim the intermediate basic sites through the formation of acid-base pairs (Mg^{2+} - O^{2-} or Al^{3+} - O^{2-}) [10]. The formation of bicarbonate anions is usually associated with surface hydroxyl groups, which are considered weak acidic or basic sites depending on the abundance of Al in the composition [10].

Using CO_2 temperature programmed desorption (TPD) measurements some authors have tried to describe the type of carbonate species, which binds on or into the hydrotalcite-type compounds. Generally, the carbonate species, which desorb at lower temperatures (100-130^{o}C), are bicarbonates species formed on Brønsted OH groups. A desorption peak at about 190-200^{o}C is associated with bidentate carbonates formed on metal-oxygen pairs. The peaks observed at higher temperatures (>280^{o}C) are usually associated with monodentate carbonate released from low-coordination oxygen anions [10, 11].

The current study aims to evaluate the contribution of weak and medium basic sites onto the CO_2 sorption capacity of two different materials, Mg/Al and Mg/Al/Zr, respectively, prepared using different techniques. Various aspects have been investigated including the activation temperature, moisture content of the gas stream or testing procedure.

Normally, the hydrotacites are known to be able to retain the carbon dioxide as carbonate species at the level of the interlayer space after an activation at elevated temperatures (>450^{o}C). This will offer access to all three types of basic sites present within these structures. The present study investigates the possibility to reduce the overall costs of the CCS process by reducing the activation temperatures and targeting only specific basic sites - weak and medium strength sites. As it will be shown the ability of the material to retain the CO_2 from an aqueous stream is in strong correlation with the different structural changes undergone by the materials during the heating treatment.

Nomenclature

sccm	standard cubic centimetres per minute
CCS	carbon capture and storage
c	cell parameter
c'	individual stacking defined by *c*/n or basal spacing
d	basal distance
MEA	monoethanol anime
MS	mass spectrometer
n	stacking sequence
TPD	temperature programmed desorption
TGA	thermal gravimetric analyzer
TSA	temperature swing adsorption
XRD	x-ray diffraction

2. Experimental Procedure

2.1. Hydrotalcite Preparation

The materials investigated in this study were prepared by MEL Chemicals using two different techniques. Sorbent DK (MELSorb XZO2025/01) was prepared using a variation of the standard co-

precipitation at constant pH method (Method A), while sorbent DM (MELSorb XZO2022/02) was prepared using a method formally called titration method (Method B). Sorbent DM has in composition Mg and Al in a molar ration of 3:1, whilst sorbent DK has in composition Mg, Al and Zr in a molar ratio of 3:0.9:0.1. The solid structure of the materials was investigated by powder x-ray diffraction (XRD). For this purpose a Philips PW3710 diffractometer with a Ni-filtered Cu K_α radiation was used. Total surface areas were measured by N_2 adsorption/desorption at 77K using a Coulter SA 3100 instrument after a degasification at 90°C for 30 minutes of the fresh materials. Particle size distribution was investigated by dynamic light scattering using a Microtrac X100 instrument. Prior measurement the samples were dispersed in a dispersant solution and sonicated at 40W for 60 seconds.

2.2. CO_2 and H_2O Uptake Measurement Procedure

An initial screening was performed on a series of samples having various compositions and it involved the utilization of a specialized fixed bed reactor using a synthetic flue gas. Using an automated system a series of adsorption/regeneration cycles under flow rates of 400ml/min were carried out.

The variation of the CO_2 and H_2O content of the gas stream was monitored using a continuous NDIR sensor. The composition of the synthetic flue gas was 12% CO_2, 4%O_2 with a balance of N_2. The moisture level was controlled using a heated bubbler within the range of 0% - 50% relative humidity (or 0-7% by volume). A temperature swing with a N_2 purge gas was used to regenerate the sorbent and desorb the CO_2. By keeping constant all the other parameters, only the regeneration temperature was varied and the adsorbed CO_2 was measured. Based on this screening two samples were selected for further investigations.

A Perkin-Elmer Pyris 1 thermogravimetric analyzer (TGA) was employed to conduct CO_2 and H_2O loading measurements at ADA-ES's laboratory, under a range of temperatures (500°C to 40°C) and CO_2 partial pressures (0, 0.15, 0.5, and 0.81 bar). The CO_2 partial pressure within the TGA assembly was controlled using CO_2/N_2 gas blends. A Hiden Analytical mass spectrometer (MS) was used to measure the gas concentration immediately above the sample of sorbent. When included, the moisture levels were approximately 1.5% by volume. Note that the TGA experiments conducted at the ADA-ES laboratory in Highlands Ranch, CO, (elevation 1643 m) were operated at less than standard atmospheric pressure; therefore with 100% CO_2, the atmospheric pressure was calculated to be 0.81 bar. In the cases where moisture was added to the gas stream, the moisture was added by passing 40 vol% of the gas through a bubbler at ambient temperature.

For the CO_2 loading experiments the procedure was the same for all the CO_2 partial pressures. Approximately 3 to 5 mg of the hydrotalcite MEL chemical material was loaded into the TGA sample pan. The gas flow rate was 100 sccm for all TGA experiments. The sample was activated either at 150°C or 500°C in the TGA under a N_2 atmosphere with approximately 1.5 vol% H_2O; this condition was held for 60 minutes. In the case of the 500°C activation the temperature was decreased to 150°C, still under a moist N_2 atmosphere and was maintained at this condition for 60 minutes. In the case of experiments completed with an activation temperature of 150°C the total activation step was 120 min instead of 60 min. After 120 minutes (total experiment time) the sample weight was recorded and considered the initial weight (i.e. no CO_2 adsorbed). After the initial weight was recorded the N_2 purge the gas was switched to either a N_2/CO_2 blend or pure CO_2, depending on the desired CO_2 partial pressure, still at 150°C and 1.5 vol% H_2O. Then, after 90 minutes the temperature was decreased by 10°C. The temperature was decreased in 10°C increments until the final temperature of 40°C was reached. The incremental increase in weight at the end of each 90 minute step was recorded as the CO_2 (or H_2O) loading at the test temperature and CO_2 partial pressure. An example of the weight gain and temperature measured during a TGA experiment with a CO_2 partial pressure of 0.15 bar is provided in Fig.1.

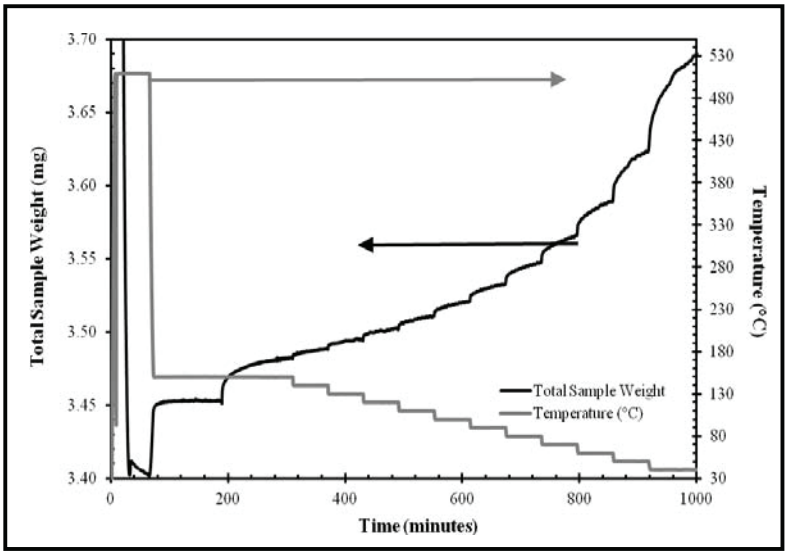

Fig. 1. Sample of weight gain and temperature recorded during a TGA experiment at a CO_2 partial pressure of 0.15 bar with 1.5 vol% H_2O

The moisture uptake was measured on the TGA for temperatures 150°C to 40°C. The general test conditions were similar to that described above to measure the CO_2 loading, but no CO_2 was included in the sample gas. Approximately 3 to 5 mg of the hydrotalcite was placed in the TGA sample pan. The activation temperature was 500°C and all other conditions regarding the activation step were the same as described previously. The weight was measured at the end of the activation step was considered to be the initial sample weight (i.e. no H_2O adsorbed). The temperature was then decreased to 150°C for 120 minutes; the weight was recorded at the end of the 120 minutes. The weight gained during each step was attributed to the adsorption of N_2 and H_2O. The temperature was decreased in 10°C increments and held at each subsequent temperature for 60 minutes; the minimum temperature was 40°C.

It has been reported that hydrotalcite-type materials can exhibit increased CO_2 adsorption in the presence of moist gas compared to dry gas [5]. However, a TGA is not the best instrument to distinguish between the weight gain due to CO_2 uptake and the weight gain due to H_2O uptake. Therefore, a fixed bed was used to measure the breakthrough curves for CO_2 after the sample had already been exposed to H_2O in N_2. The flow rate of the simulated flue gas was approximately 20 sccm, and the amount of sorbent in the reactor was 0.105 g. The sorbent and flue gas were contacted in a fixed bed through a sequence of temperature controlled lines and manual valves. A mass spectrometer was used to measure breakthrough curves of multiple gases simultaneously. The sorbent was activated before it was placed into the fixed bed. Throughout all steps of the breakthrough test approximately 4% moisture by volume was added directing gas through a bubbler at a temperature of 26°C. First, the sorbent was exposed to moist N_2 at 150°C. Then, the sorbent was cooled to 40°C in the presence of the moist N_2. The simulated flue gas, composing of approximately 18.5% CO_2, 6% O_2, with a balance of N_2 was first sent through the bypass until the initial concentration was measured. When the CO_2 reading stabilized at the known CO_2 concentration (i.e. baseline reading), the gas was directed through the sorbent and the CO_2 breakthrough curve was recorded. The breakthrough curve was integrated to calculate the CO_2 adsorbed. Note that the N_2 in the fixed bed system during the CO_2 breakthrough was taken into account.

3. Results and Discussion

3.1. Structural information

The main features of the two materials investigated here are presented in Table 1.

Table 1. Characteristics of the sorbents used in the study

Material		Sorbent DM MELSorb XZO2022/02	Sorbent DK MELSorb XZO2025/01
Cationic composition		Mg,Al	Mg, Al, Zr
S_{BET} (m^2/g)[a]		18	32
TPV (cm^3/g)		0.28	0.17
PSD	d_{10} (μm)	0.96	2.19
	d_{50} (μm)	3.17	3.93
	d_{90} (μm)	10.77	6.71
CO_2 capacity (mmol/g) at 80°C		1.84	1.71

The incorporation of Zr in a Mg/Al hydrotalcitic structure impacts several parameters, but as the topic of the paper is not related to them, only the main one is mentioned, which is the distortion introduced at the level of octahedral layer through the replacement of a smaller cation as Al^{3+} (0.053 Å) with a larger cation like Zr^{4+} (0.072 Å) which is obvious at the level of XRD patterns (not presented here) which show broader diffraction lines. This is then translated in an increase of the surface area as Zr content increases (Table 1).

Even though there are debates of whether large tetravalent cations, such as Zr and Ti, can be accommodated by the brucite type layers justified by using various investigation techniques, we have used primarily only the XRD technique to look at the variation of the lattice parameters. Hydrotalcite type compounds have specific features, usually showing strong basal reflections, which can be indexed assuming a rhombohedral symmetry. The basal reflections seen in a difractograme correspond to successive orders of the basal spacing *c'*. This parameter can be estimated easily from the XRD pattern using the formula below:

$$c' = (d_{003} + d_{006} + \ldots + nd_{00(3n)})/\mathrm{n}$$

The value of *c'* is used to calculate the cell parameter *c* which defines the stacking sequence (n) and which is 3*c'* for rombohedral and 2*c'* for hexagonal sequences. It is known that *c* parameter in the hydrotalcitic structures depends on a series of factors such as anion size, hydration and amount of interlayer anion. The incorporation of Zr in the interlayer space is expected to generate an increase of the *a* cell parameter value due to the replacement of a smaller cation such aluminium with a bigger cation and a trend following the Vegard's law has been confirmed by S. Velu et al.[12]. Though the increase in the *a* cell parameter value was not observed by D. Tichit et al. [13] . We have also investigated the variation of the cell parameters with the Zr content and found that by using either Method A or B it is difficult to obtain a direct dependence as this parameter depends on various factors and the experimental procedures weren't the same. Lattice parameter *a* instead shows a ascendant trend when Zr content is increased in the case of both synthetic methods Fig.2.

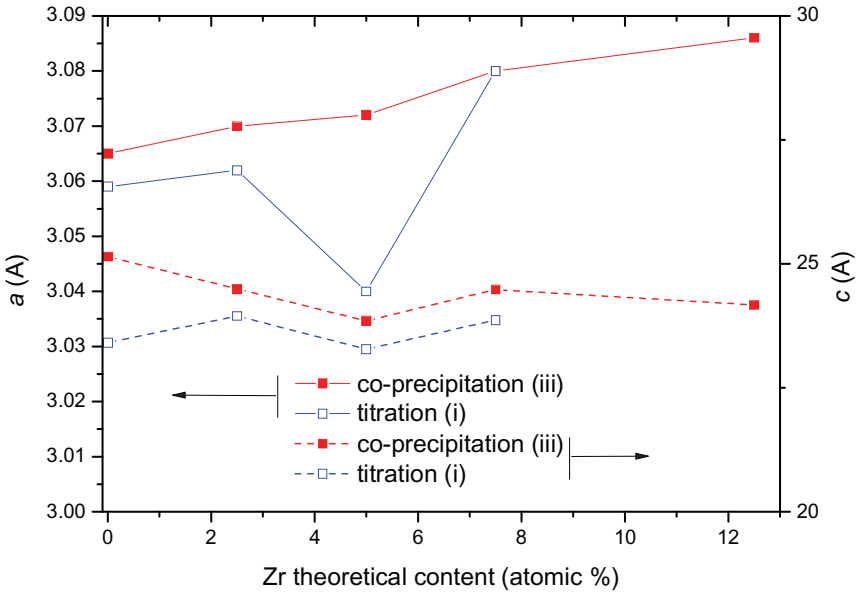

Fig.2. Evolution of *a* and *c* cell parameters with Zr content.

3.2. CO_2 adsorption characteristics

Two hydrotalcites, referred to as DK and DM, were evaluated. Because this research is ongoing a complete data set are not available for either of these materials. Therefore, the following discussion includes results measured on both materials. The work in this manuscript is still ongoing with two sorbents, DK and DM, that were chosen based on the initial CO_2 loading results Fig.3.

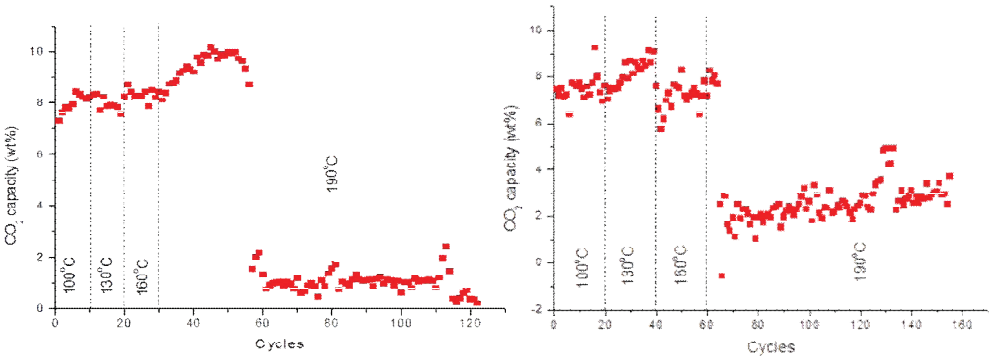

Fig. 3. Initial screening results obtained for catalysts MELSorb XZO2022/02 (left) and MELSorb XZO2025/01 (right) at 80°C.

For these tests the material was initially activated at 500°C prior CO_2 adsorption experiments. This was required in order to ensure that the material is free of any other foreign species which may be present within the structure (nitrate anions) from the precipitation stage. The resulted experimental data indicated that the hydrotalcites can show in certain conditions higher than expected CO_2 capacities. These conditions involve specific activation temperatures between the cycles. When activated at temperatures up to 160°C can exhibit capacities above 7wt% which are in strong correlation with the structural characteristics resulted during the thermal treatment. Above 160°C the capacities drop due to further structural changes mainly associated with the dehydration and dehydroxylation processes. The fact that the activity of MELSorb XZO2022/02 can be temporarily extended to 190°C is in good agreement with the TGA and TPD/MS information obtained for this sample (not presented here) which showed that this material is capable of dehydration at higher temperatures than MELSorb XZO2025/01.

The CO_2 loading at a CO_2 partial pressure of 0.15 bar for sorbent DK and DM are provided in Fig. 4 and were measured on the TGA after an activation at 500°C. Clearly, under the conditions tested the CO_2 uptake for the two sorbents is similar.

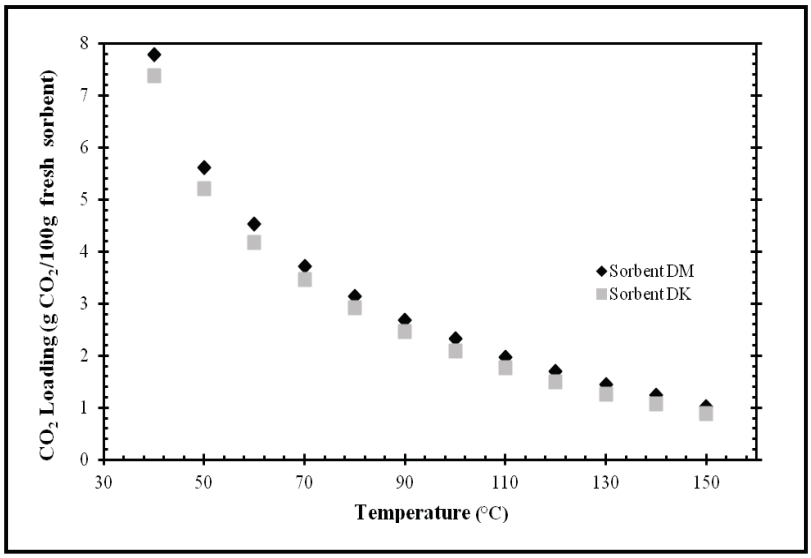

Fig. 4. Comparison of sorbent DK and DM CO_2 loading at a CO_2 partial pressure of 0.15 bar and 1.5 vol% H_2O

3.3. Activation Temperature

As has been reported by others [5], it is important to optimize the initial activation conditions for hydrotalcite-type materials. For sorbent DM, the CO_2 adsorption was measured after two different activation temperatures, 150°C and 500°C. The CO_2 loading was measured at a CO_2 partial pressure of 0.15 bar with 1.5 vol% H_2O at several different temepratures is provided in Fig. 5. From this data it is clear that the activation temperature of 150°C was not high enough.

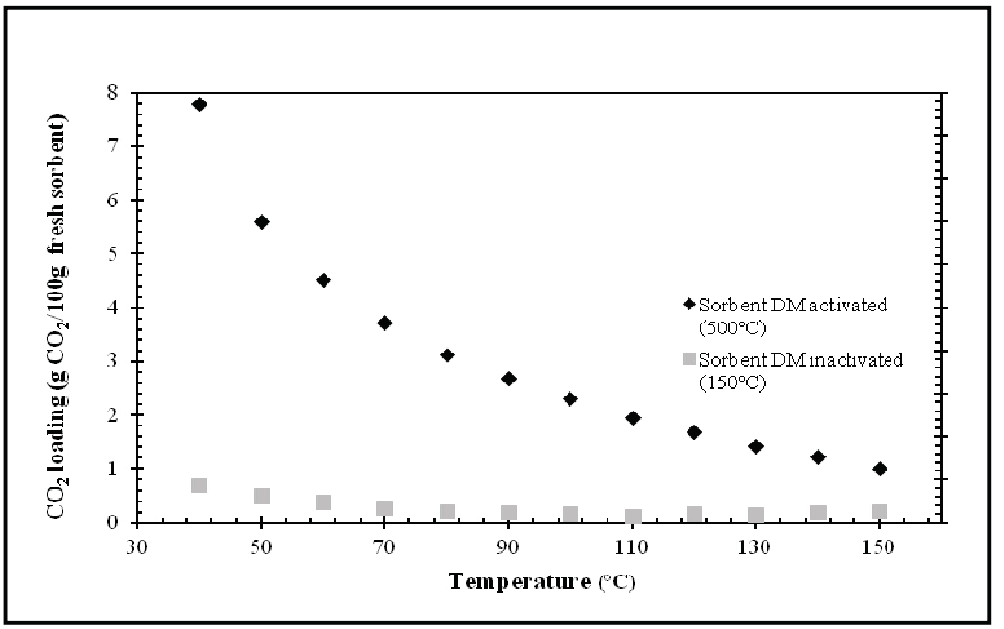

Fig. 5. Weight gain measured with activation temperatures of 150 and 500°C for Sorbent DM a CO_2 partial pressures of 0.15- bar with 1.5% H_2O

These data indicated that the initial activation of the sorbent prior to any CO_2 experiment is essential and can be correlated with the utilization as starting material of the mixed oxides obtained during the calcination. This calcination led to a template which can be functionalized as desired by controlling the composition of the gas stream prior to tests with CO_2. If the material is activated only at 150°C only a dehydration step would have a place, the material containing in the interlayer space vary species (carbonate and nitrate anions and water). The activation at higher temperatures will basically free up the basic sites which can easily be accessed by the species present in a gas stream.

3.4. Moisture

For the TGA experiments discussed in previous sections the H_2O concentration in the gas was relatively low to avoid biasing the weight gain with larger amounts of moisture. However, it has been shown that it is necessary to have some moisture in the CO_2 containing gas stream, because the CO_2 loading is poor without it. However, it is important to confirm that the weight gain measured in the TGA is primarily due to the uptake of CO_2, rather than H_2O. Also, it is of value to understand the relationship of the CO_2 and H_2O adsorption (i.e. competitive, complementary, etc.). For these reasons breakthrough curves were measured using a fixed bed for sorbent DM. The concentration of the CO_2 and the H_2O, as measured by the mass spectrometer, are provided in Fig. 6.

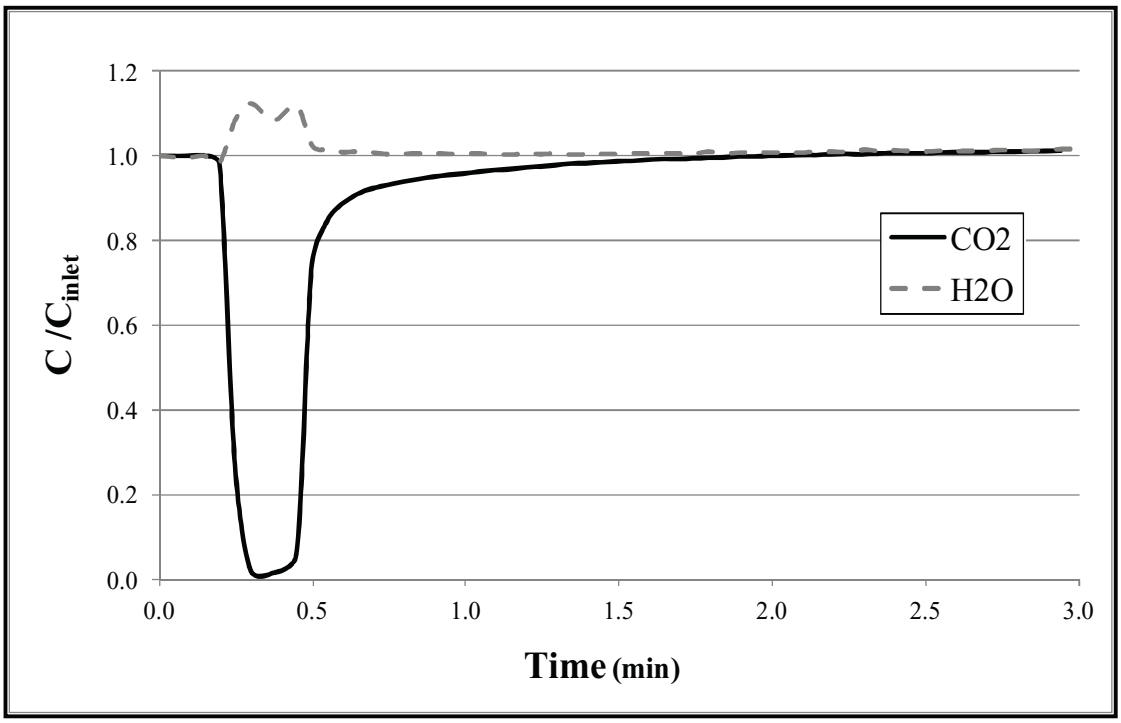

Fig. 6. Breakthrough curve of CO_2 and H_2O Measured on sorbent DM in a fixed bed

The necessity of moisture to be present in the gas stream can be linked to the formation of certain basic sites. As described in the introduction, the carbonate ions can bind to the surface of the brucite layers in three ways – monodentate, bidentate or as bicarbonate. The quantity of strong basic sites, associated with the monodentate carbonate binding, is smaller and can be reactivated only by calcination at elevated temperatures. The operation at higher temperatures will be made only based on these strong sites and the CO_2 capacities will be lower. The access to weak and intermediate-strength basic sites is facilitated by low activation temperatures and according to our findings their exploitation leads to higher CO_2 capacities. Moreover, the weak basic sites are generated only through material re-hydroxylation which can be achieved by introducing moisture in the gas stream either at the same time with CO_2 or during the activation step. The work described here aims to target the weak basic sites formed in the presence of water and to check what would the impact of a higher valence cation onto the overall reactivity. Zr^{4+} does

not seem to impact the overall capacity of the materials. Previous studies performed by MEL Chemicals (not showed here) have indicated an increase of the CO_2 capacity of the materials at high temperatures (450°C) as Zr content was increased up to 10 cationic molar percentage.

The test procedure was such that the hydrotalcite-type material was exposed to moisture in the presence of N_2 before the CO_2 was introduced. The CO_2 breakthrough curve was integrated to determine the CO_2 adsorbed by the hydrotalcite DM. The total CO_2 adsorbed was calculated to be approximately 7 g/100 g fresh sorbent, which is approximately 12% lower than the weight gain measured during the TGA experiment shown in Fig. ~~Fig.~~4. One important conclusion from this set of experiments is that at low H_2O concentration the TGA can be utilized to effectively measure the CO_2 loading at different temperatures and partial pressures.

While the presence of H_2O is important for CO_2 capture using hydrotalcite-type materials, the actual amount adsorbed in the presence of CO_2 is low when the concentration of H_2O is small (i.e. 1.5 vol% as was the case for the TGA tests). Note that during the concentration of the H_2O appears to increase during the breakthrough of the CO_2. The increase in H_2O is actually only due to the removal of CO_2; the total molar flow rate of the H_2O did not change when the CO_2 was introduced into the system. Therefore, the adsorption of CO_2 and H_2O is not competitive (i.e. H_2O was not evolved when CO_2 was introduced and the CO_2 loading was similar to that measured using the TGA). While the presence of H_2O may be necessary for CO_2 to be adsorbed, the introduction of CO_2 to a material already saturated with H_2O did not result in any additional uptake of H_2O.

4. Conclusions and Future Work

Hydrotalcite-type materials have demonstrated some valuable properties for CO_2 capture. By targeting the weak basic sites formed during the interaction of the mixed oxides, obtained through the calcination of the hydrotalcites, with the water present in a gas stream, higher CO_2 capacities were observed. These materials are of interest because they are less easily degraded at high temperature compared to some supported amine sorbents. However, the research completed to date on hydrotalcites that could be used at post-combustion temperatures is ongoing and there is still a significant amount of work that should be completed. For example, the kinetics, uptake of H_2O, enthalpy of adsorption, cost and physical properties should all be evaluated.

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